Gas-Chromatographic Separation of Hydrogen Isotopes Mixtures on Capillary Molecular Sieve 5A Column

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Gas chromatography is a method for separating components of mixtures of volatile compounds. In most applications, the separations are made to identify and determine the quantity of each component of the sample of the mixture and analytical gas chromatographic apparatus includes additional devices for this purpose. The method for separating the isotopic species of hydrogen on a moderately large scale using low temperature gas chromatography. In this paper, this method is proposed for the analysis of gas mixtures containig hydrogen isotopes. The species isotopic of hydrogen are: H_2, D_2, T_2, HD, HT, DT, where D stands for ^{2}H and T for ^{3}H. The method is based on the substantial difference in the thermal conductivity of these isotopes.

Key Words: Gas chromatography, Isotopic species of hydrogen, Mixture, Thermal conductivity, Cappilary molecular sieve 5 Å.

INTRODUCTION

The quantitative analysis of hydrogen isotopes is of great importance of separating processes of hydrogen isotopes.

Gas chromatographic separation of hydrogen isotopes have been reported in the literature dating from the late 1950's. Basically, three approaches have been employed to effect separations on an analytical scale and these approaches may be distinguished on the basis of the column packing material used.

Gas-chromatography is considered to be the most appropriate of many analytical techniques used to determine the composition or purity of gases. But, in case of hydrogen species, to determine isotopic distribution in a hydrogen isotopes mixture is too difficult because the differences among

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theirs physical-chemical properties are very small. The most differently are theirs masses and mass-spectrometry, as an analytical method, seems to be quite appropriate. However, the appearance of atomic ions, the impossibility to distinguish between two ions with the same masses and β decay of Tritium with appearance of ^{3}He are some disadvantages of this method. These disadvantages led to other analytical methods, like gas chromatography, to be considered and developed[1,2].

Three different column packing materials have been reported for the gas chromatographic separation of hydrogen isotopes. These are molecular sieves used for size exclusion chromatography, alumina used for gas/solid adsorption chromatography and palladium such as palladium dispersed on alumina used for catalytic adsorption chromatography.

The carrier gas for conducting the gas chromatographic separation of hydrogen isotope species on molecular sieves must not interact strongly with the column packing so as to adversely modify the retention of the analytes. This rules out argon which absorbs very strongly on molecular sieves at temperatures below -20 °C, however helium or neon do not interact strongly with molecular sieves at temperatures as low as -180 °C and therefore, may be used.

EXPERIMENTAL

The gas chromatograph employed in this work was a type 3800 from Varian analytical instrument.

The Varian 3800 gas-chromatograph is equipped with a capillary molecular sieve 5A column with following characteristics:

- The length of the GC column is: 50 m;
- The inside diameter of the GC column is: 0,32 mm;
- The film thickness of the GC column is: 30 μm.

The operating temperature of the GC column was 173 K (-100 ºC).

The temperature of the oven of the GC column was mainted in the range of 0-100 °C, by spraying liquid nitrogen into the oven. A temperature controller to control the liquid nitrogen flow and the heater was used[3].

As detector, we used a thermal conductivity detector TCD.

The carrier gas used was: Neon.

The sample loops: 50 μL and 5 μL.

Molecular sieves are used commonly in chromatographic applications to separate gases such as helium, hydrogen, argon, oxygen, nitrogen, methane and carbon monoxide[4]. Water, carbon dioxide and hydrocarbons are highly retained by molecular sieves. Oxygen and nitrogen are completely retained by molecular sieves at -50°C and hydrogen is retained below -180 °C.

The GC column was conditioned before to use this for the separate of the hydrogen isotopes mixtures.

RESULTS AND DISCUSSION

The method described in this study, was based on using a capillary molecular sieve 5A column which has been operated at only 173 K. The retention times were relatively short, about 8-9 min and the result is a good separation of H_2, HD, D_2. The carrier flow rate was varied from 10 to 3 mL/min in order to study how the separation efficiency varies with the flow rate.

The conclusions were that the separation efficiency is more good as the flow rate is lower (Fig. 1), but at too low flow rates the retention times were too high and peaks were large.
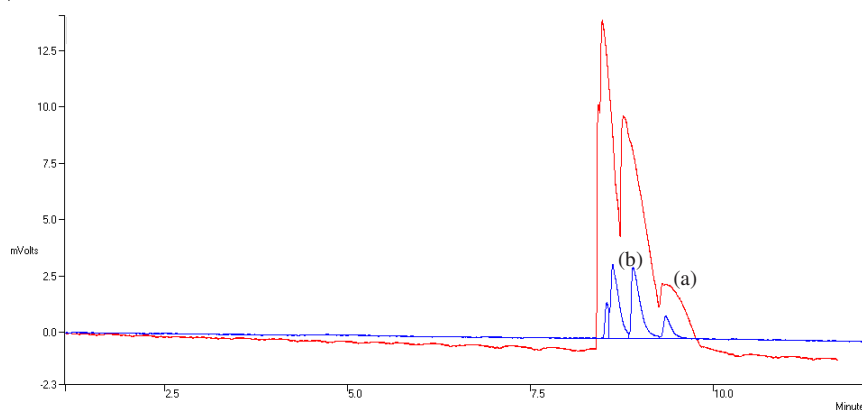

Fig. 1. (a) 50 μL Sample loop; (b) 5 μL Sample loop

Two sample loops were used in this study, *i.e.* 50 and 5 μL.

On chromatograms showed in this study (Fig. 2), is shown that the separation efficiency is more good when the sample loop (therefore the amount of sample) is small.

Various chromatograms are presented in the study for various parameters and three hydrogen isotope mixtures.

Injections of samples were made by a gas-valve coupled on-line with a isotopic exchange column and two hydrogen isotopic mixtures were available to analyze.

Another sample has been prepared by electrolyses of heavy water.

These three samples used in our experiment were:

    (a) 70.13 % H_2, 26.64 % HD and 3.21 % D_2;
    (b) 47.05 % H_2, 41.62 % HD and 11.32 % D_2;
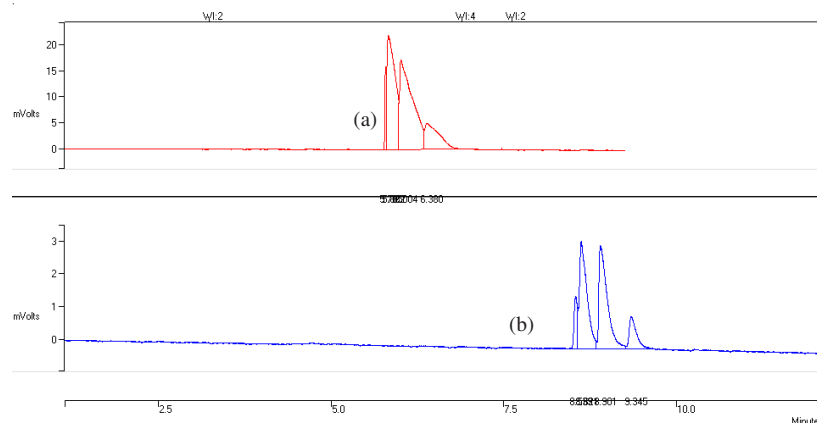   (c) 2 % HD and 98 % D_2.

Fig. 2. (a) 10 mL/min flow rate; (b) 6 mL/min flow rate

Before the gas mixture get in the sample loop, it was purified by a battery with a catalytic reactor used to reduce amount of oxygen existing in the gas mixtures, a molecular sieve adsorber used to reduce moisture and a liquid nitrogen trap[5].

The chromatograms presented in this paper demonstrate a good separation performance for capillary molecular sieve 5A column at only 173 K, in case of hydrogen species.

With this method the hydrogen species expected in an isotopic catalytic exchange column or in a cryogenic distillation column, that are used for hydrogen isotopes separation, can be separated with a quite good efficiency in a relatively short time and the analytical problems can be resolved.

A separation of *ortho*H_2-*para*H_2 is also observed, but the results are not satisfactory.

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